Kinetic Routes of PFAS Destruction in Supercritical Water Oxidation

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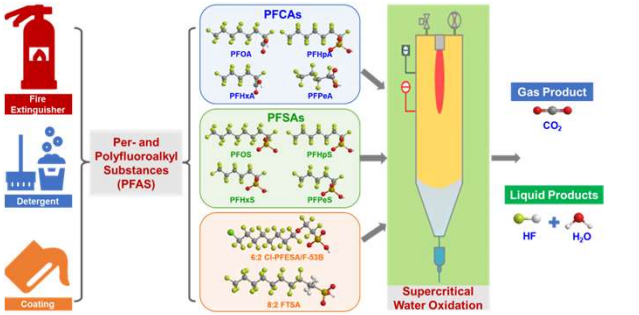
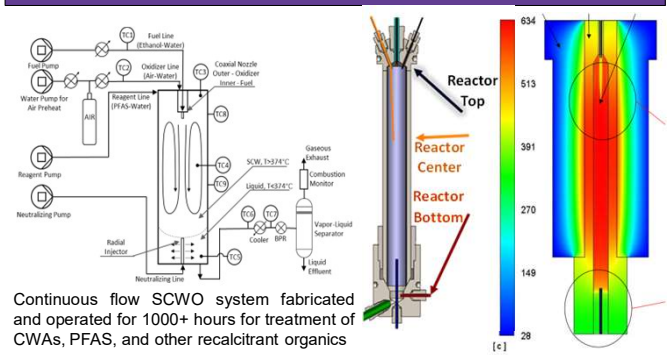
Abstract



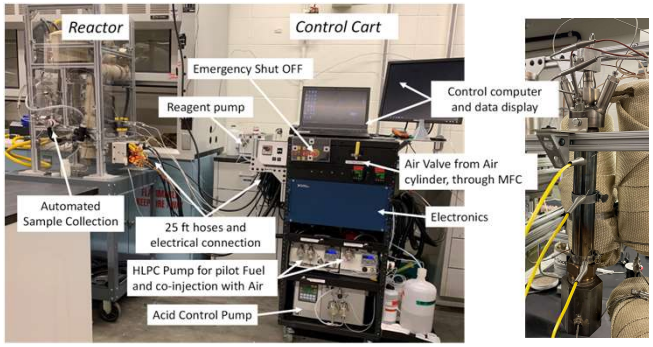
Supercritical water oxidation (SCWO) leverages high temperature, high pressure, and high oxidative radical concentrations to destroy PFAS and organic contaminants

UW Continuous Flow SCWO Reactor Design



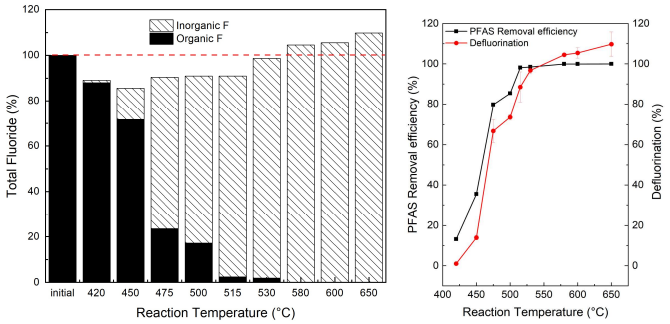
Continuous flow SCWO system fabricated and operated for 1000+ hours for treatment of CWAs, PFAS, and other recalcitrant organics

Benchtop SCWO System



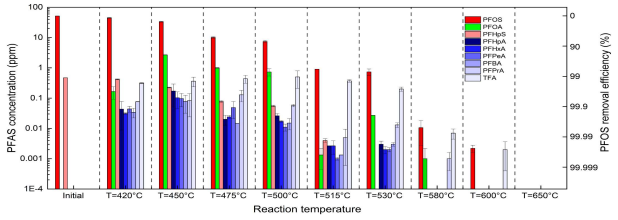
Autogenic operation is established by custom control hardware and software. Control of pilot fuel (ethanol) and air flow rate determine temperature and the residence time.

PFOS Destruction and Defluorination



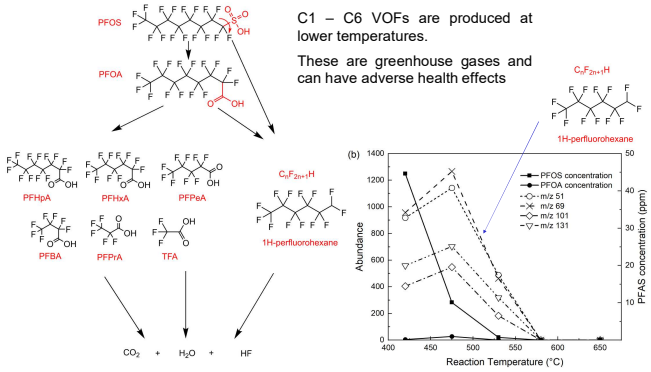
Defluorination lags destruction at lower T, suggesting formation of unidentified intermediate volatile organofluorine (VOF) compounds

PFOS Intermediates



PFOS decomposition yields formation of PFCAs found in the effluent (LC-MS/MS) followed by chain shortening, including C2-C6 PFCAs. DRE > 99.999% at 650 °C

PFOS Reaction Mechanism



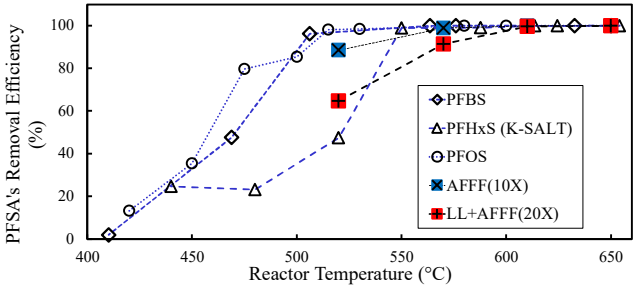
C1 – C6 VOFs are produced at lower temperatures.

These are greenhouse gases and can have adverse health effects

Conclusions

- **Autogenic operation in lab scale continuous SCWO reactor for 1000+ hours**
- **Established operational envelop for the destruction of PFAS matrices**
- **No PFAS or intermediates are found at 650 °C; residence time ~30 s**

PFAS Matrix Destruction and Defluorination



Landfill Leachate + AFFF matrix is the most recalcitrant of tested compounds. Temperature of >610 °C is required -- higher that neat PFOS or AFFF.

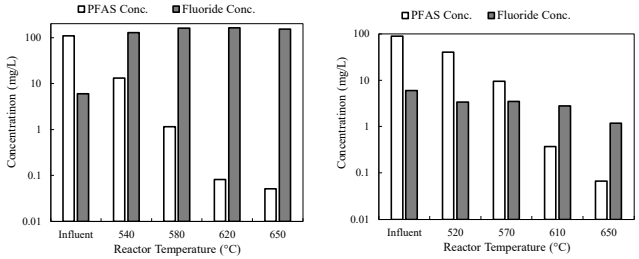
Gas Production in SCWO

Reagent		VOF Produced	
Name	Formula	Name	Formula
PFOS	$C_8F_{17}SO_3H$	1H-perfluoroheptane	$C_7F_{15}H$
PFOA	$C_7F_{15}COOH$	1H-perfluoroheptane	$C_7F_{15}H$
PFBS	$C_4F_9SO_3H$	1H-perfluoropropane*	C_3F_7H
PFBA	C_3F_7COOH	1H-perfluoropropane*	C_3F_7H
TFA	CF_3COOH	Fluoroform	CF_3H
TFMS	CF_3SO_3H	No Gas	No Gas

*The identity of individual VOFs is not confirmed due to the similarity of 1H-perfluoroalkanes mass spectra and a lack of GC libraries

F-Balance for PFAS Matrix

AFFF (10X dilute) **AFFF (20X dilute) + Landfill Leachate**



Tested landfill leachate matrix shows lower fluorine conversion. The landfill leachate suppresses free fluoride in the effluent, ~1% of organic fluorine is recovered.

Acknowledgements

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